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Sublimation enthalpies of 9 substituted acetanilides at 298 K estimated by solution calorimetry approach

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ABSTRACT

In this work a solution calorimetry approach was applied for determination of the sublimation enthalpies of 9 substituted acetanilides. The solution enthalpies of acetanilide and 9 its derivatives in acetonitrile were measured and solvation enthalpies were calculated by a group-additivity scheme. Additivity of solvation enthalpy due to influence of the substituent on the acidity of the proton of $NHCOCH_3$-group and OH-group was checked with the use of IR-spectroscopy. The sublimation enthalpies obtained from the solution calorimetry approach were compared to the available literature data. In most cases convergence within the limits of experimental uncertainty was demonstrated.

1. Introduction

Acetanilide derivatives are actively used in the chemical and pharmaceutical industry. Compounds based on acetanilide possess a wide spectrum of physiological activity, including analgesic and antipyretic, anesthetic, antiarrhythmic and nootropic properties [1,2]. Substituted acetanilides are intermediate products in the synthesis of dyes [3]. Acetanilide derivatives have been the object of sustained research in perspective drugs design over the last decades [4–7].

Sublimation enthalpies of acetanilide derivatives are necessary for quantification of their solvation enthalpies in different solvents. Hydration enthalpies of biologically active compounds are important values in understanding of their bioavailability [8]. On the other hand, sublimation enthalpies at 298.15 K together with combustion calorimetry data lead to formation enthalpies in gas phase. Sublimation enthalpies of substituted acetanilides were obtained by gas saturation method in [9] (acetanilide, 4′-hydroxyacetanilide, 4′-ethoxyacetanilide), [10] (4′-hydroxyacetanilide), [11] (2′-hydroxyacetanilide, 3′-hydroxyacetanilide), [12] (2′-, 3′- and 4′- carboxyacetanilides); Knudsen effusion method in [13] (acetanilide, 2′-methylacetanilide, 4′-methylacetanilide), [14] (acetanilide), [15] (4′-hydroxyacetanilide), [16] (4′-hydroxyacetanilide), [17] (2′- and 3′-carboxyacetanilides), [18] (4′-carboxyacetanilide) and its modifications in [19] (4′-ethoxyacetanilide); Calvet-drop sublimation calorimetry in [16] (4′-hydroxyacetanilide). Additionally, vapor pressures of liquid acetanilide derivatives and the vaporization enthalpies were studied in [20] (4′-ethoxyacetanilide, 4′-bromoacetanilide, 4′-hydroxyacetanilide) by thermogravimetric analysis; in [21] (acetanilide, 3′-ethoxyacetanilide, 4′-ethoxyacetanilide, 4′-methoxyacetanilide, 4′-methylacetanilide) by correlation gas chromatography; in [22] (4′-methoxyacetanilide, 4′-ethoxyacetanilide) by isoteniscope. Unfortunately, sublimation enthalpies values obtained in the above mentioned studies are often in disarray. Such discrepancies may be due to low volatility of acetanilides, which necessitates carrying out the measurements at elevated temperatures and sometimes above the melting point. In the absence of standards for the calibration under these conditions, the experimental results are not as reliable as at the lower temperatures [23].

Recently [24,25] we developed the method of determination of sublimation and vaporization enthalpies of aromatic compounds from experimentally measured solution enthalpies and calculated solvation enthalpies. Solution calorimetry procedures are carried out at ambient conditions. This technique does not face the problems related to thermal instability of the sample or require vapor pressure measurements at elevated temperatures. In addition, there is no need to adjust the experimental data to the standard temperature (298.15 K). Another important advantage of the solution calorimetry approach over conventional methods of sublimation enthalpy determination is the lower demands on the purity of the samples. In the present study we determine sublimation enthalpies of substituted acetanilides with the help of solution calorimetry combined with a solvation enthalpy group-additivity scheme [24].

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